



Short communication

Synthesis and electrical property of $\text{Li}_{2-x}\text{FeSi}_{1-x}\text{P}_x\text{O}_4$ as positive electrodes by spark-plasma-sintering process

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HIGHLIGHTS

- A single phase of $\text{Li}_{2-x}\text{FeSi}_{1-x}\text{P}_x\text{O}_4$ was prepared by Spark-plasma-sintering process.
- The electrical conductivity was improved by the replacing $(\text{SiO}_4)^{4-}$ with $(\text{PO}_4)^{3-}$.
- An ionic character by the localized 3d electron of Fe was encouraged.

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ABSTRACT

$\text{Li}_{2-x}\text{FeSi}_{1-x}\text{P}_x\text{O}_4$ was prepared with the intention of improving the electrical conductivity by taking advantage of the high lithium ionic conductivity of $\text{Li}_4\text{SiO}_4\text{--Li}_3\text{PO}_4$ solid solution. A monoclinic single phase by SPS process was obtained for $x = 0, 0.1$ and 0.2 in $\text{Li}_{2-x}\text{FeSi}_{1-x}\text{P}_x\text{O}_4$ and the process produced the samples in high dense in half an hour while their containing less than 3% of carbons. The electrical conductivity was increased by the replacing $(\text{SiO}_4)^{4-}$ with $(\text{PO}_4)^{3-}$, although the conductivity value itself was not reliable due to the carbon. The electrochemical properties of the samples using Li were evaluated and showed a slight improvement on the rate performance. A desired tetrahedral divalent Fe was confirmed in all investigated samples and ionic character caused by the localized 3d electron of Fe in the structure was encouraged by the complexation.

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1. Introduction

Recently, Li-ion batteries have been expected to be used as a large power source, for examples, electric vehicles. In contrast a progress in negative electrodes has been made, developing positive electrodes with high capacity is crucial. Li_2MnO_3 -based positive electrodes such as $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ have been extensively investigated [1–3]. They have a combined superior character of large capacity, *ca.* 200 mAh g⁻¹ and good thermal stability, and consequently, are one of the best candidates with high energy density. However, material design based on the element strategy without any rare metals is also an important issue.

LiFePO_4 material has been proposed one of the promising positive electrodes using abundant Fe with less toxicity [4]. Although

this material originally shows a poor electronic conductivity due to the localized 3d electrons of Fe in the olivine structure consisting of the framework of $(\text{PO}_4)^{3-}$, it has been used as a practical positive electrode in the Li-ion batteries. This electrode can work until treatments are provided such as carbon-coating or pulverizing powders of the active material. However, an enlargement of the rechargeable capacity has achieved a threshold value corresponding to 1 mol of Li theoretically. Therefore, the materials including a large amount of Li will be a target compound, such as Li_2MnO_3 -based or $\text{Li}_2\text{FeSiO}_4$ electrodes [5].

Investigations on improving the electronic conductivity of LiFePO_4 by doping have been already performed [6]. Therefore, we have examined to improve the ionic conductivity of poly anion-based materials by complexation, and evaluate the effect on the electrochemical performances. Focusing on complex oxo-acid salts with excellent pure Li ionic conductivity, $\text{Li}_4\text{SiO}_4\text{--Li}_3\text{PO}_4$ ($\text{Li}_{4-x}\text{Si}_{1-x}\text{P}_x\text{O}_4$) system has been adopted. For this system an excellent works by West et al. are available [7–9]. Based on their results,

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followed by the reinvestigation on the phase relationship and the electrical conductivity of the system and then introducing Fe or Mn into the system were examined. The composition of the investigated compounds can be represented as $\text{Li}_{2-x}\text{FeSi}_{1-x}\text{P}_x\text{O}_4$ and could be expected to exhibit both ionic and electronic conductivity.

In this research, we have conducted the following plans based on the idea described above: (1) preparations and measurements of the materials with high Li ion conductivity and without electronic conductivity; (2) introducing Fe or Mn into the pure Li ionic conductor; (3) evaluation the electrochemical properties as positive electrode. Additionally, the potential to prepare positive electrodes by spark-plasma-sintering (denoted as SPS in the following) method was examined. Takeuchi et al. have succeeded in producing dense LiFePO_4/C composite using SPS process [10]. They are not aimed to prepare the LiFePO_4 directly, but a composite with carbon by SPS. However, it usually needs several hours to prepare poly anion-based electrodes such as by hydrothermal process. The SPS method can reduce the preparation time drastically and avoid the oxidation effectively, because the samples are inserted with die made of carbon in vacuum during SPS process [10,11]. A schematic view of SPS process is shown in Fig. 1. Furthermore, the SPS process may produce a new metastable phase because of its characteristics rapid heating process [12]. However, it should be noted that there is a possibility for organic compounds to remain as carbons if organic acid salts are used as starting materials.

Here, we present that the obtained samples by SPS process was a single phase for $x = 0, 0.1$ and 0.2 in $\text{Li}_{2-x}\text{FeSi}_{1-x}\text{P}_x\text{O}_4$ in less than an hour. Moreover, the effect of the complexation on the structure, electrical conductivity and electrochemical properties will be discussed.

2. Experimental

The samples of Li_4SiO_4 – Li_3PO_4 system ($x = 0$ – 1.0 with 0.1 interval in $\text{Li}_{4-x}\text{Si}_{1-x}\text{P}_x\text{O}_4$) were prepared by solid state reaction (denoted as SS) and SPS process. For the former, Li_2CO_3 , amorphous SiO_2 and $\text{NH}_4\text{H}_2\text{PO}_4$ were mixed by agate mortar, pelletized and calcined at 473 and 973 K for 12 h. After grinding the obtained samples, they were pelletized again and followed by sintering at 1273 K for 3 days. During this sintering process a crucible including excess of Li_2CO_3 was installed in the furnace in which the pelletized samples were placed. By this treatment Li vapor will be filled in the furnace and prevent for Li to evaporate from the samples during heating. For the SPS process, heat treatments before sintering were

in the same manner as SS. Then, obtained samples were sintered by the SPS apparatus (Dr. Sinter, Model SPS-1020, Sumitomo Coal Mining, Japan): heating rate of 4 – 100 °C min $^{-1}$; holding time of 5–30 min; holding temperature at 873–1073 K.

The samples of $\text{Li}_{2-x}\text{FeSi}_{1-x}\text{P}_x\text{O}_4$ ($x = 0$ – 1.0) were prepared by SPS and hydrothermal methods (HR). For the former, chemical grade of Li_2CO_3 , amorphous SiO_2 , $\text{NH}_4\text{H}_2\text{PO}_4$ and $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ were mixed, pelletized and then they were heated up to 1173 K at 300 °C min $^{-1}$ and hold for 5–15 min in 10^{-3} Pa vacuum. For HR, the starting materials were chemical grade $\text{LiOH} \cdot \text{H}_2\text{O}$, amorphous SiO_2 , $\text{NH}_4\text{H}_2\text{PO}_4$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$. The samples were obtained followed by hydrothermal reaction at 423 K for 72 h.

The phase identification of obtained samples was performed by CuK_α radiation and the Rietveld refinements were carried out. The ac impedance was measured using a frequency-response analyzer over a frequency range 4– 10^6 Hz with an applied potential of 0.10 V under N_2 atmosphere. Electrochemical measurements using coin-type cells were carried out galvanostatically at 298 and 333 K by HJ1001SD (HOKUTO DENKO, Ltd., Japan). The positive electrode material was composed of the sample, acetylene black and polyvinylidene fluoride (PVdF) in 70:25:5 wt% ratio. Li metal was used as a negative electrode and the electrolyte was 1 M LiPF_6 in ethylene carbonate (EC):1,2-dimethoxycarbonate (DMC) in a 1:1 volume ratio.

3. Results and discussion

3.1. Preparation of $\text{Li}_{4-x}\text{Si}_{1-x}\text{P}_x\text{O}_4$

To begin with we examined the composition without Fe which is pure Li ionic conductor, commonly referred to as a solid electrolyte. The samples were prepared by spark-plasma-sintering (SPS) method and for comparison, the conventional solid state reaction (SS) to recognize the phase relationship of Li_4SiO_4 and Li_3PO_4 system which is available in the literature [8]. The chemical composition was controlled precisely by depressing the loss of Li as described in the Experimental section. XRD patterns of the samples by both the preparations apparently showed a single monoclinic phase arising from Li_4SiO_4 phase in the range of $x = 0$ – 0.4 in $\text{Li}_{4-x}\text{Si}_{1-x}\text{P}_x\text{O}_4$ and a single orthorhombic phase arising from Li_3PO_4 in the range of $x = 0.6$ – 1.0 . However, the sample of $x = 0.5$ prepared by solid state reaction showed two phases consisting of Li_4SiO_4 and Li_3PO_4 , whereas the sample by SPS a single orthorhombic phase. This discrepancy results from the difference sintering conditions. That of SPS is as follows: the heating rate of 573 K min $^{-1}$; heating time for 15 min at 1173 K. On other hand, the solid state reaction requires 3 days at 1273 K for the sintering. Although the SPS process can significantly reduce the sintering period, the obtained samples are in a metastable state. The compositional dependence on the lattice parameters showed a formation of solid solutions between Li_4SiO_4 and Li_3PO_4 , in which Si was replaced by P. The solid solution region seems to be wider than those reported in the past [8]. The literature have described that Li_4SiO_4 forms an extensive range of metastable solid solutions containing up to $x = 0.6$. The details on the phase relationship of the Li_4SiO_4 – Li_3PO_4 system prepared by SPS will appear later.

3.2. Ionic conductivity of $\text{Li}_{4-x}\text{Si}_{1-x}\text{P}_x\text{O}_4$

The representative results of the electrical conductivity obtained by the complex impedance measurement were shown in Fig. 2. The electrical conductivity for all the samples was higher than those of two end members. The Arrhenius plots of the electrical conductivity may indicate an absence of the phase transition in the investigated temperature ranges of 573–973 K. The

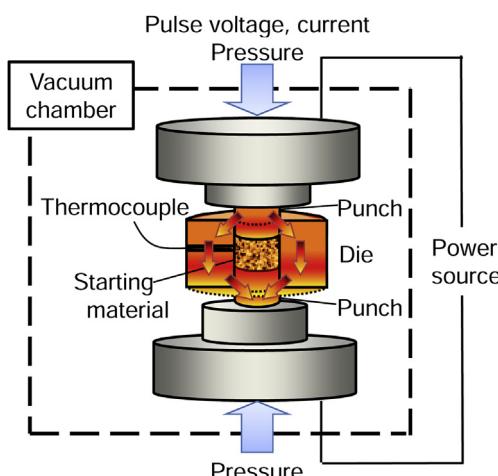


Fig. 1. A schematic view of spark-plasma-sintering process.

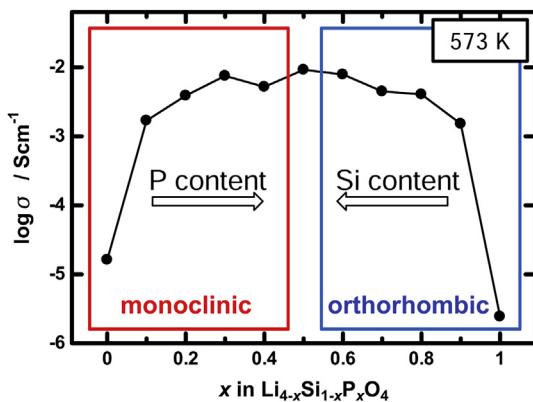


Fig. 2. The compositional dependence on the isothermal electrical conductivity at 573 K measured by impedance spectroscopy for $\text{Li}_{4-x}\text{Si}_{1-x}\text{P}_x\text{O}_4$.

calculated activation energy for the ionic conduction in the system ranged from 0.4 to 0.6 eV for SS and SPS. However, the conductivity of $x = 0.5$ by SPS was slightly higher than that of by SS due to the improved sintered density. It is known that the complex salts of Li_4SiO_4 – Li_3PO_4 exhibits much higher electrical conductivity than those of two end members, Li_4SiO_4 and Li_3PO_4 [8,13,14]. They have an ordered structure concerning Li^+ ions, thus exhibiting a very low ionic conductivity. The reason why the complex salts indicate high ionic conductivity can be explained by using both the increasing the concentration of Li-vacancy up to $x = 0.5$ as shown in $\text{Li}_{4-x}[\text{V}_{\text{Li}}]\text{P}_x\text{Si}_{1-x}\text{O}_4$ using Kröger Vink notation and the additional mobile Li^+ ions as a carrier on the interstitial site based on the structure of Li_3PO_4 .

It is interesting that the sintered samples prepared by SPS process were transparent due to the favorable sintered density. This was confirmed by the observed impedance spectra which a ratio of the contribution by grain boundary resistance to bulk one was reduced.

3.3. Preparation of $\text{Li}_{2-x}\text{FeSi}_{1-x}\text{P}_x\text{O}_4$

We attempted to introduce Fe into the composition of $\text{Li}_{3.5}\text{Si}_{0.5}\text{P}_{0.5}$ with the highest conductivity by replacing two Li sites by one divalent Fe. A desired single phase was not obtained, but mixed with monoclinic $\text{Li}_{4-x}\text{Si}_{1-x}\text{P}_x\text{O}_4$ and Fe_3O_4 phases appeared. Consequently, we decided to investigate the compositions of $x = 0$ – 0.5 in $\text{Li}_{2-x}\text{FeSi}_{1-x}\text{P}_x\text{O}_4$ including fixed divalent Fe. Fig. 3 shows XRD patterns for $x = 0$ – 0.5 in $\text{Li}_{2-x}\text{FeSi}_{1-x}\text{P}_x\text{O}_4$ prepared by SPS method.

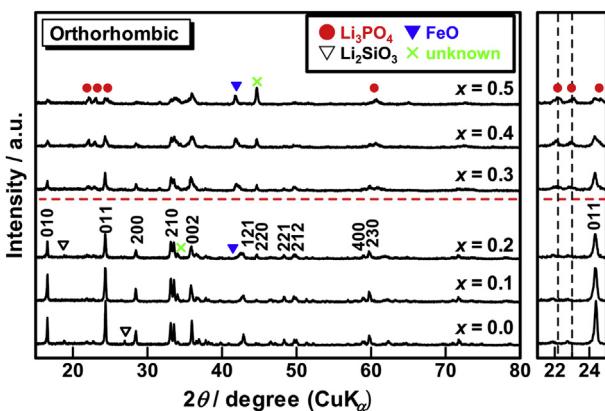


Fig. 3. XRD patterns for $\text{Li}_{2-x}\text{FeSi}_{1-x}\text{P}_x\text{O}_4$ prepared by the SPS process.

The SPS apparently produced a single phase ranging from $x = 0$ to 0.2 in $\text{Li}_{2-x}\text{FeSi}_{1-x}\text{P}_x\text{O}_4$, although a small amount of impurities Li_2SiO_3 and FeO phases were observed. In the samples beyond $x = 0.2$, the peaks corresponding to Li_3PO_4 phase significantly appeared in addition to unknown phase. It was recognized that the samples included a significant amount of residual organic by thermal decomposition of Fe-oxalates or carbon inserted by dies although such phases were no longer distinguishable by XRD measurement. These residuals result in making the apparent color of the samples black. Then, the black products on the samples prepared by SPS were deleted mechanically. Then, TG-DTA analysis was performed and the amount of carbons in the samples was estimated to be less than 3%. There was no outstanding difference in the XRD patterns for the samples prepared by the hydrothermal reaction in which the reaction time was for 72 h at 423 K by using an autoclave. However, it should be noted that the SPS method can produce a single phase in less than an hour. For comparison, the preparation by the conventional solid state reaction is currently under investigation. It is necessary to sinter the sample for 72 h at 973 K to obtain a single phase.

An investigation has been reported recently on a similar composition, represented as $\text{Li}_{1-x}\text{Fe}_{1+x}\text{P}_{1-x}\text{Si}_x\text{O}_4$ [15]. A complete solid solution between Triphyllite and Fayalite olivine structures has been formed. On the other hand, our target is the compounds containing more than 1 mol of Li and two different poly anions, $(\text{SiO}_4)^{4-}$ and $(\text{PO}_4)^{3-}$ focusing on their high ionic conductivity, as shown in Fig. 2.

3.4. Electrical conductivity

Fig. 4 shows the Arrhenius plots of the electrical conductivity for the sintered $\text{Li}_{2-x}\text{FeSi}_{1-x}\text{P}_x\text{O}_4$, measured at a temperature range from 298 to 473 K. The electrical conductivity was increased linearly with increasing temperature and the isothermal electrical conductivity of the samples over all investigated temperatures increased with content of P. It should be noted that the absolute value of σ was not reliable. The obtained electrical conductivity of $\text{Li}_2\text{FeSiO}_4$ prepared by SPS was much higher than reported to be around $\sigma \approx 6 \times 10^{-14} \text{ S cm}^{-1}$ at room temperature [16]. The activation energy from these results was calculated to be around less than 0.1 eV for $x = 0.2$. This value is much lower for the ionic conduction and there is obviously an influence of the carbons containing in the samples. As described earlier, our samples contain less than 3% of the formed carbons during sintering process which will govern the electrical conductivity. However, the tendency of the change in the conductivity by replacing Si by P is worth remarking on. The amount of carbons in all investigated samples

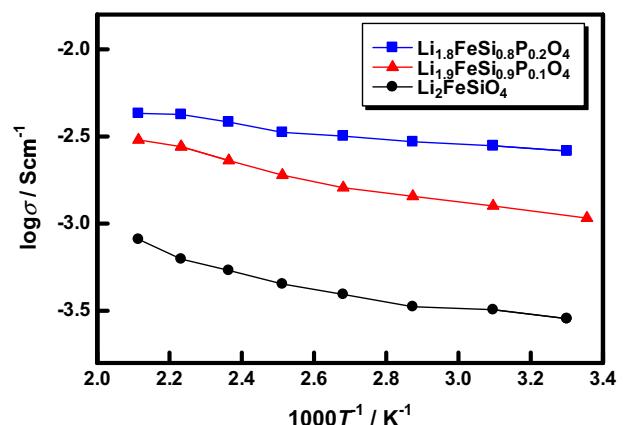


Fig. 4. Arrhenius plots of the electrical conductivity for $\text{Li}_{2-x}\text{FeSi}_{1-x}\text{P}_x\text{O}_4$ prepared by the SPS process.

was almost the same. Therefore, the replacing $(\text{SiO}_4)^{4-}$ with $(\text{PO}_4)^{3-}$ in $\text{Li}_2\text{FeSiO}_4$ resulted in increasing the total electrical conductivity. The effect on the chemical bonding properties with respect to localized 3d electrons of Fe will be discussed later.

3.5. Electrochemical properties

The obtained powders by SPS process were ball-milled in air at the beginning and then charge–discharge tests using Li were carried out. Consequently, a reversible capacity corresponding to one electron was obtained for all the samples, $x = 0, 0.1$ and 0.2 in $\text{Li}_{2-x}\text{FeSi}_{1-x}\text{P}_x\text{O}_4$ without any plateau at around 3.0 V.

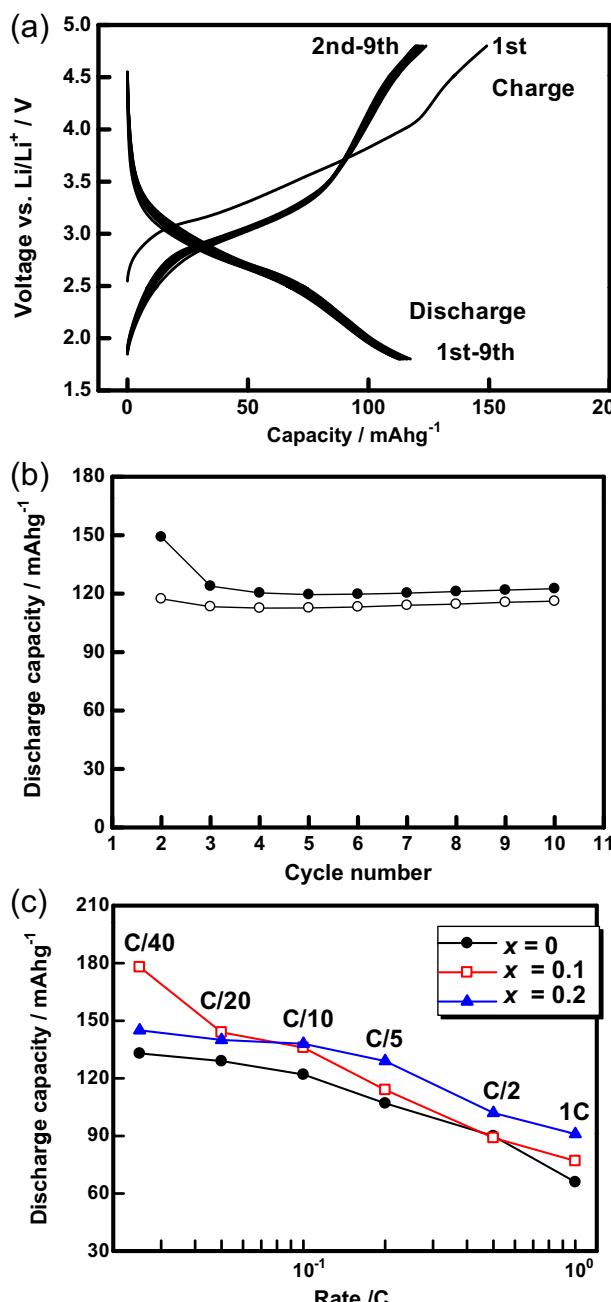


Fig. 5. A representative results of charge and discharge tests using Li of $\text{Li}_{1.8}\text{FeSi}_{0.8}\text{P}_{0.2}\text{O}_4$ prepared by the SPS method, measured at 333 K: (a) charge–discharge curves with 1/40 C and cut-off voltages of 1.8 and 4.8 V, (b) relationship between discharge capacity and cycle number up to 10 cycles and (c) rate performance at various current densities.

Subsequently, the powders were ball-milled in Ar atmosphere and then, the charge–discharge curves of $x = 0.2$ changed as shown in Fig. 5(a) and (b). There is a clear plateau associated with a redox of divalent Fe at around 3.0 V [5,17] and a reversible specific capacity of 120 mAh g^{-1} corresponding to 0.85 M Li . Therefore, it was found that the investigated samples are very sensitive for environmental atmosphere and must be treated carefully to avoid the oxidation of Fe.

On the other hand, it seems that there are no distinguish effects of the improved electrical property on the electrochemical performances, although a slight improvement on the rate performance was obtained as shown in Fig. 5(c). We need more information on the electrochemical properties of the complex oxo-salts-based electrodes prepared by the SPS process.

3.6. Mössbauer spectroscopy

The obtained samples prepared by SPS were examined by ^{57}Fe Mössbauer spectra at room temperature in order to investigate the chemical states of Fe in the samples. A desired tetrahedral divalent Fe was confirmed in all investigated samples, in addition to a considerable amount of impurity phases consisting of FeO and Fe_3O_4 . The results of the analysis by fitting showed that there was a monotonous change in the isomer shift and FWHM of the target by the substitution of Si by P. These results can be explained by the change of chemical bonding properties based on the inductive effect. By introducing the framework of $(\text{PO}_4)^{3-}$ into that of $(\text{SiO}_4)^{4-}$, a covalent character of poly anions will be increased. Consequently, an ionic bonding character between Fe and O will be increased by the inductive effect. Therefore, localized 3d electron of Fe in the structure may be encouraged. These results agreed with those obtained by the electrical conductivity measurements; the complexation with $(\text{PO}_4)^{3-}$ and $(\text{SiO}_4)^{4-}$ enhances the ionic bonding character and the increased electrical conductivity is responsible for not 3d electrons of Fe, but mobile Li^+ ions. However, the further investigation is presently underway to clarify changes in chemical bonding of Fe caused by the substitution of Si for P using the samples without any impurity phases. The details on the results of Mössbauer spectroscopy will appear in the near future.

4. Summary

The SPS process produced a single phase for $x = 0, 0.1$ and 0.2 in $\text{Li}_{2-x}\text{FeSi}_{1-x}\text{P}_x\text{O}_4$ successfully in less than an hour. The sintered samples were in enough dense and were able to be discussed the electrical conductivity. The electrical conductivity was increased by the replacing $(\text{SiO}_4)^{4-}$ with $(\text{PO}_4)^{3-}$, although the conductivity value itself was not reliable due to the less than 3% carbons containing in the samples. The electrochemical performance of the samples showed a slight improvement on the rate performance. A desired tetrahedral divalent Fe was confirmed in all investigated samples and ionic character caused by the localized 3d electron of Fe in the structure was encouraged by the complexation.

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